Form PTO-1390 (REV 10-95) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER 388-001287 U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/600195
INTERNATIONAL APPLICATION NO. PCT/JP98/05676	INTERNATIONAL FILING DATE 16.12.98 (December 16, 1998)	PRIORITY DATES CLAIMED 13.01.98 (January 13, 1998)

TITLE OF INVENTION **A METHOD OF SELECTIVELY REFORMING AN INNER PART OF AN INORGANIC BODY AND AN INORGANIC BODY HAVING A SELECTIVELY REFORMED INNER PART**

APPLICANT(S) FOR DO/EO/US
Kiyotaka MIURA, Jianrong QIU, Yuki KONDO and Kazuyuki HIRAO

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1 ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.

3 ☒ This express request to begin national examination procedures (35 U.S C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).

4 ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5 ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))

a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).

b ☒ has been transmitted by the International Bureau.

c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).

6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).

7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U S C. 371(c)(3))

a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).

b ☐ have been transmitted by the International Bureau.

c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.

d. ☒ have not been made and will not be made.

8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S C. 371(c)(3)).

9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12 ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. ☒ A FIRST preliminary amendment.

☐ A SECOND or SUBSEQUENT preliminary amendment

14 ☐ A substitute specification

15 ☐ A change of power of attorney and/or address letter.

16. ☒ Other items or information:

a. WO 99/36171-Front Page with Abstract and Search Report (2 pp.)
b. Written Opinion and Reply - English translation thereof
c. English translation of International Preliminary Examination Report completed 06 January 2000

534 Rec'd PCT/PTO 12 JUL2000

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/600195	PCT/JP98/05676	2204-001287

17. ☒ The following fees are submitted:

		CALCULATIONS PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):		
Search Report has been prepared by the EPO or JPO.....	**$840.00**	
International preliminary examination fee paid to USPTO (37 CFR 1.482)	**$670.00**	
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....	**$760.00**	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO.....	**$970.00**	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4).....	**$96.00**	
ENTER APPROPRIATE BASIC FEE AMOUNT =		$ 840.00
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		$ 0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	14 - 20	0	X **$18.00**	$ 0.00
Independent claims	2 - 3 =	0	X **$78.00**	$ 0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$260.00**	$ 0.00
TOTAL OF ABOVE CALCULATIONS =				$ 840.00
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				$ 0.00
SUBTOTAL =				$ 840.00
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$ 0.00
TOTAL NATIONAL FEE =				$ 840.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 40.00
TOTAL FEES ENCLOSED =				$ 880.00
				Amount to be: refunded $
				charged $

a. ☒ A check in the amount of $ **880.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of $ _____ to cover the above fees
A duplicate copy of this sheet is enclosed.

c. ☒ The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-0650 . A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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REGISTRATION NUMBER

PATENT APPLICATION/PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:	ATTORNEY DOCKET NUMBER
Kiyotaka MIURA, Jianrong QIU, Yuki KONDO and Kazuyuki HIRAO	2204-001287

PCT/JP98/05676

ENTITLED

"A METHOD OF SELECTIVELY REFORMING AN INNER PART OF AN INORGANIC BODY AND AN INORGANIC BODY HAVING A SELECTIVELY REFORMED INNER PART"

To BOX PCT
Attention: DO/EO/US

Assistant Commissioner for Patents
Washington D.C. 20231

EXPRESS MAIL CERTIFICATE

"Express Mail" Label Number EL561552403US

Date of Deposit July 12, 2000

I hereby certify that the following attached paper or fee

PRELIMINARY AMENDMENT with ABSTRACT

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. §1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Kara A. Toward
(Typed name of person mailing paper or fee)

Kara A. Toward
(Signature of person mailing paper or fee)

PATENT APPLICATION
Attorney Docket No. 2204-001287

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	:	
Kiyotaka MIURA,	:	**A METHOD OF SELECTIVELY**
Jianrong QIU,	:	**REFORMING AN INNER PART**
Yuki KONDO,	:	**OF AN INORGANIC BODY AND**
and Kazuyuki HIRAO	:	**AN INORGANIC BODY HAVING**
		A SELECTIVELY REFORMED
International Application	:	**INNER PART**
No. PCT/JP98/05676	:	
International Filing Date	:	
16 December 1998	:	
Priority Date Claimed	:	
13 January 1998	:	
Serial No. Not Yet Assigned	:	
Filed Concurrently Herewith	:	

Pittsburgh, Pennsylvania
July 12, 2000

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

Preliminary to a first Office Action on the merits, please amend the above-identified application in the manner indicated below.

IN THE SPECIFICATION:

Page 1, line 1, delete "SPECIFICATION".

Page 1, line 6, delete "TECHNICAL FIELD OF THE INVENTION" and substitute therefor:

--BACKGROUND OF THE INVENTION

1. Field of the Invention--.

Page 1, line 12, delete "BACKGROUND OF THE INVENTION" and substitute therefor

--2. Background Art--.

Page 2, line 17, after "from" insert --the--.

Page 2, line 20, after "Such" insert --that--.

Page 3, line 12, delete "PREFERRED EMBODIMENT OF THE PRESENT INVENTION" and substitute therefor --DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS--.

Page 3, line 14, after "overlap" insert --the--.

Page 3, line 15, after "including" insert --the--.

Page 5, line 10, delete "60 minutes".

Page 5, line 11, after "H_2-N_2" insert --for 60 minutes--.

Page 5, line 16, delete "Presence" and substitute therefor --The presence--.

Page 5, line 17, delete "the".

Page 5, line 21, after "and" insert --a--.

Page 5, line 21, after "1kHz" delete "a".

Page 6, line 8, delete "Presence" and substitute therefor --The presence--.

Page 6, line 12, after "that" insert --the--.

Page 6, line 20, after "YF_3," insert --and--.

Page 6 line 25, delete "a".

Page 6, line 28, delete "Presence" and substitute therefor --The presence--.

Page 7, line 1, delete "the".

Page 7, line 4, after "and" insert --a--.

Page 7, line 4, before "repetition" delete "a".

Page 7, line 11, delete "The" and substitute therefor --A--.

Page 7, line 13, after "ions" insert --was used--.

Page 7, line 19, after "and" insert --a--.

Page 7, line 19, before "repetition" delete "a".

Page 8, line 13, delete "the" (second occurrence) and substitute therefor --a--.

IN THE CLAIMS:

Please cancel claims 1-7, cancel amended claims 1-7, and add new claims 8-21 as follows:

--8. A method of selectively reforming an inner part of an inorganic body, which comprises:

emitting a pulsed laser beam of wavelength different from the absorption wavelength of rare earth and/or transition metal ion to an inorganic body containing said rare earth and/or transition metal ion, and

condensing said pulsed laser beam at a focal point in an inner part of said inorganic body, whereby said rare earth and/or transition metal ion changes its valence only at said focal point and its vicinity.

9. The method of selectively reforming an inner part of an inorganic body defined in claim 8, wherein the inorganic body is a glass or crystal containing one or more selected from the group consisting of metal oxides, metal halides and metal chalcogenides.

10. The method of selectively reforming an inner part of an inorganic body defined in claim 8, wherein the rare earth ion is one or more selected from the group consisting of Ce, Nd, Pr, Sm, Eu, Tb, Dy, Tm and Tb ions.

11. The method of selectively reforming an inner part of an inorganic body defined in claim 8, wherein the transition metal ion is one or more selected from the group consisting of Ti, Mn, Cr, V, Fe, Cu, Mo and Ru ions.

12. The method of selectively reforming an inner part of an inorganic body defined in claim 8, wherein the focal point is relatively shifted with respect to the inorganic body so as to form a domain with a predetermined pattern where the rare earth and/or transition metal ion changes its valence.

13. The method of selectively reforming an inner part of an inorganic body defined in claim 8, wherein the inorganic body is irradiated with a pulsed laser beam with pulse width under a picosecond.

14. An inorganic body having a selectively reformed domain in an inner part of said inorganic body wherein the valence of rare earth and/or transition metal ions is changed by condensing irradiation energy of a pulsed laser beam of wavelength different from the absorption wavelength of said rare earth and/or transition metal ion.

15. The inorganic body as claimed in claim 14, wherein said reformed domain is formed by relatively shifting the focal point of the laser beam with respect to said inorganic body so as to form a domain with a predetermined pattern.

16. The inorganic body as claimed in claim 14, wherein said inorganic body is a glass or crystal containing one or more selected from the group consisting of metal oxides, metal halides and metal chalcogenides.

17. The inorganic body as claimed in claim 14, wherein said rare earth ions are one or more selected from the group consisting of Ce, Nd, Pr, Sm, Bu, Tb, Dy, Tm and Tb ions.

18. The inorganic body as claimed in claim 14, wherein said transition metal ions are one or more selected from the group consisting of Ti, Mn, Cr, V, Fe, Cu, Mo and Ru ions.

19. The inorganic body as claimed in claim 14, wherein the irradiation energy is provided by a pulsed laser beam with pulse width under a picosecond.

20. The inorganic body as claimed in claim 14, used as a memory device.

21. The inorganic body as claimed in claim 14, used as a light-emitting device.--

IN THE ABSTRACT:

Please delete the Abstract of the Invention as currently on file and add the new Abstract Of The Invention which has been added as a separately typed page to be inserted after the claims.

REMARKS

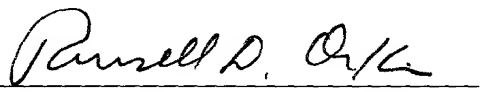
The specification has been amended to place the application in conformance with standard United States patent practice.

Original claim 1-7 have been canceled by this Preliminary Amendment and rewritten as new claims 8-14. Claims 15-21 have been added to further define the invention.

Examination and allowance of pending claims 8-21 are respectfully requested.

Respectfully submitted,

WEBB ZIESENHEIM LOGSDON
ORKIN & HANSON, P.C.

By 

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A METHOD OF SELECTIVELY REFORMING AN INNER PART OF AN INORGANIC BODY AND AN INORGANIC BODY HAVING A SELECTIVELY REFORMED INNER PART

ABSTRACT OF THE INVENTION

An inorganic body containing rare earth and/or transition metal ions that has been irradiated with a pulsed laser beam in the manner such that a focal point of the pulsed laser beam is adjusted to an inner part of the inorganic body is disclosed. The inorganic body may be a glass or crystal containing one or more of oxide, halide and chalcogenide. The rare earth ion may be one or more of Ce, Nd, Pr, Sm, Eu, Tb, Dy, Tm, Tb. The transition metal ion may be one or more of Ti, Mn, Cr, V, Fe, Cu, Mo and Ru. When the focal point is relatively shifted with respect to the inorganic body, an ionic valence-changed domain is formed with a predetermined pattern at the inner part of the inorganic body. The pulsed laser beam preferably has a pulse width under a picosecond. The ionic valence change occurs at the focal point and its vicinity, but the rare earth or transition metal ion keeps its original valence at all other parts, so as to form a reformed domain with a predetermined pattern in the inorganic body. Since optical properties are selectively changed at the reformed domain, the processed inorganic body is useful as a functional device such as a memory device or a light-emitting device using the differentiated optical properties.

SPECIFICATION

A METHOD OF SELECTIVELY REFORMING AN INNER PART OF AN INORGANIC BODY AND AN INORGANIC BODY HAVING A SELECTIVELY REFORMED INNER PART

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a method of selectively reforming an inner part of an inorganic body by irradiation with a condensed pulsed laser beam and a new inorganic body produced thereby.

BACKGROUND OF THE INVENTION

When an inorganic body containing rare earth or transition metal ion is subjected to oxidization-reduction or irradiated with an X-ray or ultraviolet beam, a valence of the rare earth or transition metal ion changes. For instance, J. Qiu et al. reported change of Eu^{2+} to Eu^{3+} by irradiating Eu^{2+}-containing fluoride with an X-ray or ultraviolet beam, in Appl. Phys. Lett.71 (1997) 759. W. A. Weyl reported change of Mn^{2+} to Mn^{3+} by irradiating Mn^{2+}-containing oxide with an ultraviolet beam, in Coloured Glasses, Society of Glass Technology (1951).

In order to realize valence change of rare earth or transition metal ion at a specified part of an inorganic body, the inorganic body is covered with a shading mask having a predetermined pattern, and then selectively irradiated with an X-ray or ultraviolet beam. The valence of the ion is partially changed at a part defined by the pattern of the shading mask.

Valence of rare earth or transition metal ion can be also changed by an oxidization-reduction method in a controlled atmosphere. In this case, valence change occurs over a whole of the inorganic body, but it is difficult to selectively change a part of the ion in the inorganic body. On the other hand, valence change of ion induced by

irradiation with a X-ray or ultraviolet beam depends on a reaction in one photon process, so that an energy of the X-ray or ultraviolet beam is absorbed in a surface layer of the inorganic body. As a result, it is difficult to selectively change valence of the ion only at an inner part of the inorganic body.

Conventional methods have difficulty for selectively changing ion valence at a specified inner part of an inorganic body, as above-mentioned.

SUMMARY OF THE INVENTION

The present invention is accomplished to overcome such the problems as above-mentioned. The present invention aims at provision of a new inorganic body improved in functionality by selective valence change of rare earth or transition metal ion at its specified inner part. The selective valence change is realized by irradiating an inorganic body containing rare earth and/or transition metal ion with a condensed pulsed laser beam of wavelength different from absorption wavelength of the rare earth and/or transition metal ion.

According to the present invention, a pulsed laser beam of wavelength different from absorption wavelength of rare earth and/or transition metal ion emitted to an inorganic body containing rare earth and/or transition metal ion in the manner such that a focal point of the pulsed laser beam is adjusted to an inner part of the inorganic body. Such the condensing irradiation induces valence change of the rare earth and/or transition metal ion only at the focal point and its vicinity.

The inorganic body may be a glass or crystal containing one or more of oxides, halides and chalcogenides. Rare earth ion may be one or more of Ce, Nd, Pr, Sm, Eu, Tb, Dy, Tm and Tb ions. Transition metal ion may be one or more of Ti, Mn, Cr, V, Fe, Cu, Mo and Ru ions.

When the focal point is relatively shifted with respect to the inorganic body, a domain with a predetermined pattern where the rare earth and/or transition metal ion changes its valence is formed at an inner part of the inorganic body. The pulsed laser

beam is with pulse width under a picosecond.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view for illustrating an inorganic body irradiated with a pulsed laser beam which is condensed at a focal point adjusted to an interior of the inorganic body.

Fig. 2 is a schematic view for illustrating a confocus optical system useful for measuring an ionic valence-changed domain.

Fig. 3 is a graph which indicates valence change of rare earth or transition metal ion by condensing irradiation with a pulsed laser beam.

PREFFERED EMBODIMENT OF THE PRESENT INVENTION

A pulsed laser beam useful in the present invention is of wavelength which does not overlap characteristic absorption wavelength of an objective inorganic body including absorption wavelength of rare earth or transition metal ion. As far as a pulse energy of 50% or more on the basis of a total irradiation energy is obtained, ionic valence change occurs only at a focal point.

A pulsed laser beam is with pulse width under a picosecond. Since a peak power of the pulsed laser beam becomes smaller as elongation of the pulse duration, a peak energy of the pulsed laser beam shall be greater in order to obtain a similar peak power density. The peak power of the pulsed laser beam is represented by a power (W) which is a divided value of an energy (J) per 1 pulse by pulse width (sec), and the peak power density is represented by a ratio (W/cm^2) of the peak power (W) to a unit area (cm^2).

Pulse width is preferably controlled within a range of 100-500 femtoseconds. If an inorganic body is irradiated with a laser beam with pulse width narrower than 100 femtoseconds, pulse width in an inner part of the inorganic body is greatly varied in response to a position of a focal point along a direction of depth, since the inorganic

body itself is a dispersion material. Consequently, it is difficult to dimensionally control a domain where ionic valence change occurs. If the pulse width is over 500 femtoseconds on the contrary, the inorganic body is likely damaged when its inner part is irradiated with a condensed pulsed laser beam with a peak energy sufficient for ionic valence change.

A pulsed laser beam 1 is condensed by a condenser lens 4 so as to position a focal point 2 at an inner part of an inorganic body 3, and emitted to the inorganic body 3, as shown in Fig. 1. When an electric field intensity of the pulsed laser beam 1 at the focal point 2 exceeds a certain threshold in response to valence change of rare earth or transition metal ion, the rare earth or transition metal ion changes its valency at the focal point 2 and its vicinity. A position apart from the focal point 2 is subjected to an electric field of intensity insufficient for occurrence of ionic valence change. As a result, the valence change of the rare earth or transition metal ion occurs only at the focal point 2 and its vicinity, and the inner part of the inorganic body 3 is selectively reformed.

A domain where such ionic valence change occurs can be shaped to a predetermined pattern by relative movement of the focal point 2 with respect to the inorganic body 3. For instance, the ionic valence-changed domain is shaped to a two- or three-dimensional pattern by shifting the focal point 2 along directions of X, Y, Z by operation of an optical system, shifting the inorganic body 3 along directions of X, Y and Z, or shifting both the focal point 2 and the inorganic body 3.

The inner part (reformed part) of the inorganic body 3 at the focal point 2 and its vicinity is the ionic valence-changed domain, while rare earth or transition metal ion at the remaining part (unreformed part) is still of its original valence. The resulting differentiated ionic valence between the reformed and unreformed parts causes differences in optical characteristics such as light absorption and light emission. The inorganic body reformed in this way is useful as a functional device such as an optical memory device, light-emitting device or amplifier device, using such the differentiated

ionic valence.

The present invention will be more apparent from the following examples. Of course, these examples do not put any restrictions on the scope of the present invention.

EXAMPLE 1

SiO_2, Na_2CO_3, Eu_2O_3 raw materials were weighed and mixed together to prepare oxide glass composition which contained cations at ratios of 73mol% Si^{4+}, 25mol% Na^+ and 2mol% Eu^{2+}. The mixture was put in a Pt crucible and melted 30 minutes at 1450°C and then cooled to a room temperature. A glass obtained in this way was received in a carbon crucible and subjected 60 minutes to a reducing reaction at 1450°C in an atmosphere of 5vol.% H_2-N_2. Thereafter, the glass melt was rapidly cooled together with the crucible to a room temperature, to obtain a Eu^{2+}-containing oxide glass.

A testpiece of 5mm in thickness was cut off the Eu^{2+}-containing oxide glass. Two planes of the testpiece were polished at an optical level and examined by spectral analysis for measuring absorption spectrum. Presence of Eu^{2+} in the oxide glass was detected by the spectral analysis.

The testpiece was then irradiated with a pulsed laser beam 1 which was condensed by a condenser lens 4 in a manner such that a focal point 2 is positioned at an inner part of the testpiece 3, as shown in Fig. 1. The pulsed laser beam was of 800nm wavelength with 300 femtoseconds pulse width and 1kHz a repetition rate oscillated from a Ti- sapphire laser excited with an argon laser.

A light beam of 400nm wavelength was emitted to and condensed at the same focal point 3 of the testpiece after being irradiated with the condensed pulsed laser beam, using a confocus optical system (shown in Fig. 2). In this confocus optical system, a laser beam 1 which held diffraction minimum penetrates a tube lens 5 and an objective lens 6, and condensed in a surface or inner part of the testpiece 3. When a condensing plane 7 is adjusted to the inner part of the testpiece 3, a light through the

condensing plane 7 penetrates the objective lens 6 and tube lens 5, and is imaged on a confocus pin-hole 9 by a beam splitters 8. Since light beams emitted from the other parts except the condensing plane 7 of the testpiece 3 are effectively separated by the confocus pin-hole 9, characteristic changes, i.e. ionic valence change, at the focal point 3 is proven from a fluorescence spectrum obtained by detecting the image formation with a photodetector 10.

Fig. 3 is a measuring result of a fluorescence spectrum (a) from a part corresponding to the focal point 2 (shown in Fig. 1). Presence of a fluorescence spectrum originated in Eu^{3+} is noted in Fig. 3. For comparison, a fluorescence spectrum from the other part except the focal point 2 was measured in the same way. In this case, a fluorescence spectrum (b) originated in Eu^{2+} was detected. It is apparently recognized by comparing these fluorescence spectra (a) and (b) that valence of Eu ion was changed from 2+ to 3+ at the focal point 2 and its vicinity by emitting the pulsed laser beam 1 to and condensing it at the inner part of the testpiece 3. The same valence change of Eu ion from 2+ to 3+ were detected by emitting a pulsed laser beam and condensing it at an inner part of another glass containing halide, sulfide or chalcogenide in the same way.

EXAMPLE 2

AlF_2, MgF_2, CaF_2, SrF_2, BaF_2, YF_3, SmF_3 raw materials were weighed and mixed together to prepare fluoride glass composition which contained cations at ratios of 35mol% Al^{3+}, 10mol% Mg^{2+}, 20mol% Ca^{2+}, 10mol% Sr^{2+}, 10mol% Ba^{2+}, 14mol% Y^{3+}, and 1mol% Sm^{2+} and an anion sole of F^-. The mixture was put in a carbon crucible and reductively melted 60 minutes at 1000°C in an atmosphere of 5 vol.% H_2-N_2. Thereafter, the glass melt was rapidly cooled together with the crucible to a room temperature.

A testpiece was cut off an obtained Sm^{2+}-containing fluoride glass. Two planes of the testpiece were polished at an optical level and examined by spectral analysis for measuring absorption spectrum. Presence of Sm^{2+} in the oxide glass was detected by

the spectral analysis.

An inner part of the testpiece 3 was subjected to condensed irradiation with a peak energy density of 10^8-10^{15}W/cm^2 using a pulsed laser beam 1 of 1100nm wavelength with 120 femtoseconds pulse width and 200kHz a repetition rate. In Example 2, the testpiece 3 was shifted at a speed of 20μm/second with respect to an optic axis of the laser beam 1.

A fluorescent spectrum at each of a part irradiated with the pulsed laser beam and a non-irradiated part was measured by excitation with a light beam of 515nm wavelength using the same confocus optical system as that in Example 1. The measurement result proved that Sm ion changed its valence from 2+ to 3+ only at a locus of the focal point 3 of the pulsed laser beam. The similar ionic valence change was recognized when a fluoride glass containing one or more of Ce, Nd, Pr, Eu, Tb, Dy, Tm, Yb, Ti, Mn, Cr, V, Fe, Cu, Mo and Ru ions.

Example 3

A testpiece 3 of 10mm in length, 10mm in width and 5mm in thickness was prepared from a single crystal having compositions of AlF_3: SrF_3: LiF=1:1:1 (a mol ratio) and containing 1mol% Ce^{3+}, and polished at an optical level. A pulsed laser beam of 550nm wavelength with 120 femtoseconds pulse width and 200kHz a repetition rate was emitted to the testpiece 3 in the manner such that the pulsed laser beam 1 was condensed at a focal point 2 adjusted to an inner part of the testpiece 3 with a peak energy density of 10^8-10^{15}W/cm^2. In Example 3, the testpiece 3 was shifted under such the irradiating condition at a speed of 20μm/second with respect to an optical axis of the laser beam 1.

A fluorescent spectrum at each of a part irradiated with the pulsed laser beam and a non-irradiated part was measured by excitation with a light beam of 300nm wavelength using the same confocus optical system as that in Example 1. The measurement result proved that Ce ion changed its valence from 3+ to 4+ along a locus

of the focal point 2, while Ce ion kept its original valence 3+ at the other part except the locus of the focal point 3. The similar valence change of Ce ion from 3+ to 4+ was detected when other crystals containing halide, oxide and/or chalcogenide were irradiated with condensed pulsed laser beams in the same way.

INDUSTRIAL APPLICATION

According to the present invention as above-mentioned, ionic valence is changed at a focal point and its vicinity in an inner part of an inorganic body containing rare earth or transition metal ion by irradiating the inorganic body with a pulsed laser beam in a manner such that the focal point of the pulsed laser beam is adjusted to the inner part of the inorganic body. The ionic valence change occurs only at the focal point and its vicinity, while the other part keeps its original ionic valence. As a result, the inorganic body is reformed to such the state that an ionic valence-changed domain is surrounded with the remaining part which keeps the original ion valence. The partial change of the ion valence differentiates optical properties such as absorption and fluorescence, resulting in selective change of the optical properties at a specified domain in the inner part of the inorganic body. The inorganic body processed in this way is useful as a functional device such as a memory device or a light-emitting device using the differentiated optical properties.

CLAIMS

1. A method of selectively reforming an inner part of an inorganic body, which comprises:

emitting a pulsed laser beam of wavelength different from absorption wavelength of rare earth and/or transition metal ion to an inorganic body containing said rare earth and/or transition metal ion, and

condensing said pulsed laser beam at a focal point in an inner part of said inorganic body,

whereby said rare earth and/or transition metal ion changes its valence only at said focal point and its vicinity.

2. The method of selectively reforming an inner part of an inorganic body defined in Claim 1, wherein the inorganic body is a glass or crystal containing one or more of oxide, halide and chalcogenide.

3. The method of selectively reforming an inner part of an inorganic body defined in Claim 1 or 2, wherein the rare earth ion is one or more of Ce, Nd, Pr, Sm, Eu, Tb, Dy, Tm and Tb ions.

4. The method of selectively reforming an inner part of an inorganic body defined in Claim 1 or 2, wherein the transition metal ion is one or more of Ti, Mn, Cr, V, Fe, Cu, Mo and Ru ions.

5. The method of selectively reforming an inner part of an inorganic body defined in either one of Claims 1 to 5, wherein the focal point is relatively shifted with respect to the inorganic body so as to form a domain with a predetermined pattern where the rare earth and/or transition metal ion changes its valence.

6. The method of selectively reforming an inner part of an inorganic body defined in either one of Claims 1 to 6, wherein the inorganic body is irradiated with a pulsed laser beams with pulse width under a picosecond.

7. An inorganic body having such the selectively reformed inner part that a domain where valence of rare earth and/or transition metal ion is changed by

condensed irradiation of a pulsed laser beam of wavelength different from absorption wavelength of said rare earth and/or transition metal ion is formed with a predetermined pattern in an inner part of said inorganic body.

ABSTRACT

An inorganic body 3 containing rare earth and/or transition metal ion is irradiated with a pulsed laser beam 1, in the manner such that a focal point 2 of the pulsed laser beam 1 is adjusted to an inner part of the inorganic body 3. The inorganic body 3 may be a glass or crystal containing one or more of oxide, halide and chalcogenide. The rare earth ion may be one or more of Ce, Nd, Pr, Sm, Eu, Tb, Dy, Tm, Tb. The transition metal ion may be one or more of Ti, Mn, Cr, V, Fe, Cu, Mo and Ru. When the focal point 2 is relatively shifted with respect to the inorganic body 3, an ionic valence-changed domain is formed with a predetermined pattern at the inner part of the inorganic body 3. The pulsed laser beam is preferably with pulse width under a picosecond. The ionic valence change occurs at the focal point 2 and its vicinity, but the rare earth or transition metal ion keeps its original valence at the other part, so as to form a reformed domain with a predetermined pattern in the inorganic body 3. Since optical properties are selectively changed at the reformed domain, the processed inorganic body 3 is useful as a functional device such as a memory device or a light-emitting device using the differentiated optical properties.

PATENT APPLICATION/PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:	ATTORNEY DOCKET NUMBER
Kiyotaka MIURA, Jianrong QIU, Yuki KONDO and Kazuyuki HIRAO	2204-001287

PCT/JP98/05676

ENTITLED

"A METHOD OF SELECTIVELY REFORMING AN INNER PART OF AN INORGANIC BODY AND AN INORGANIC BODY HAVING A SELECTIVELY REFORMED INNER PART"

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FIG.1

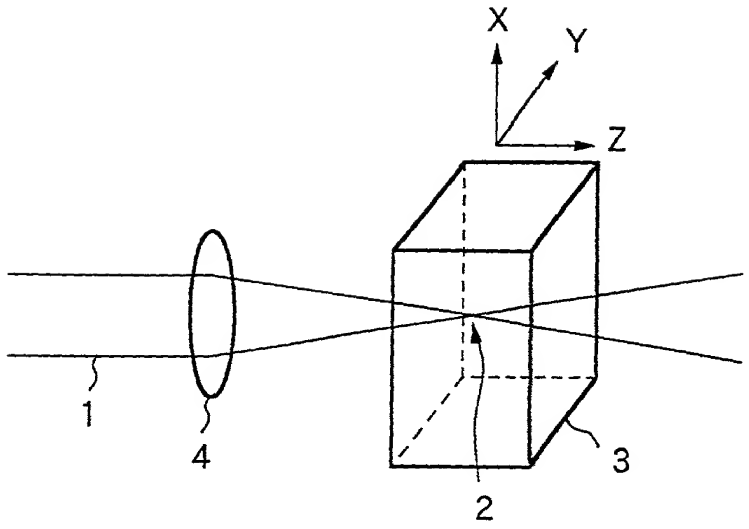


FIG.2

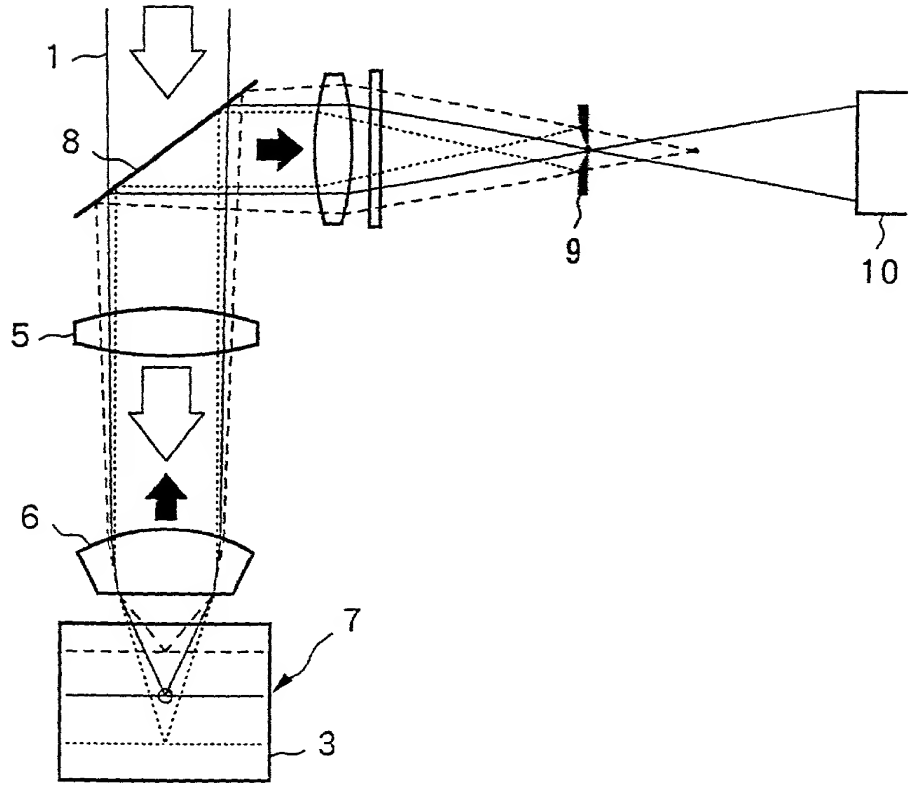
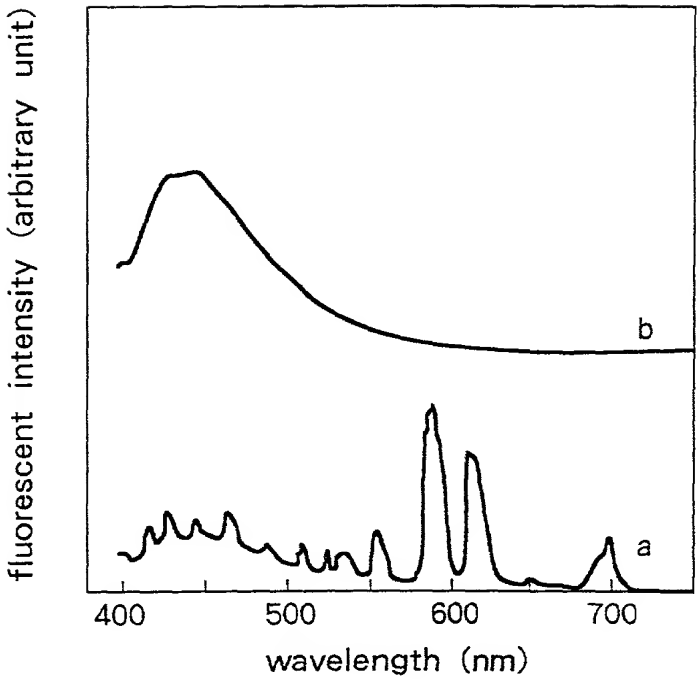


FIG.3



a : fluorescent spectrum of Eu^{3+} in a zone irradiated with a pulsed laser

b : fluorescent spectrum of Eu^{2+} in a non – irradiated zone

Declaration and Power of Attorney For Patent Application
特許出願宣言書

Japanese Language Declaration

私は、下欄に氏名を記載した発明者として、以下の 通り宣言する：

As a below named inventor, I hereby declare that:

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My residence, post office address and citizenship are as stated below next to my name.

名称の発明に関し、請求の範囲に記載した特許を求める主題の本来の、最初にして唯一の発明者である（一人の氏名のみが下欄に記載されている場合）か、若しくは本来の、最初にして共同の発明者である（複数の氏名が下欄に記載されている場合）と信じ、

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I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

A METHOD OF SELECTIVELY REFORMING AN INNER PART OF AN INORGANIC BODY AND AN INORGANIC BODY HAVING A SELECTIVELY REFORMED INNER PART

その明細書を
（該当する方に印を付す）
☒ここに添付する。
☐_____日に出願番号
第_____号として提出し、
_____日に補正した。
（該当する場合）

the specification of which
(check one)
☒ is attached hereto
☐ was filed on _____ as Application Serial No._____
and was amended on _____
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私は、前記のとおり補正した請求の範囲を含む前記明細書の内容を検討し、理解したことを陳述する。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

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I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

Prior foreign applications 先の外国出願			Priority Claimed 優先権の主張	
10-004416	Japan	13.01.1998	☒	☐
(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願の年月日)	Yes あり	No なし
			☐	☐
(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願の年月日)	Yes あり	No なし

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I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a)which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

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